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TITLE: Liquid crystalline medium

Abstract Paragraph (1):
The invention relates to a liquid-crystalline medium comprising at least one compound of the formula I 1

Abstract Paragraph (4):
Z.sup.1, Z.sup.2, Z.sup.3, a, b and c are as defined in claim 1, and to electro-optical displays containing a liquid-crystalline medium of this type.

Summary of Invention Paragraph (1):
[0001] The present invention relates to a liquid-crystalline medium, to the use thereof for electro-optical purposes, and to displays containing this medium.

Summary of Invention Paragraph (2):
[0002] Liquid-crystals are used principally as dielectrics in display devices, since the optical properties of such substances can be modified by an applied voltage. Electro-optical devices based on liquid crystals are extremely well known to the person skilled in the art and can be based on various effects. Examples of such devices are cells having dynamic scattering, DAP (deformation of aligned phases) cells, guest/host cells, TN cells having a twisted nematic structure, STN (supertwisted nematic) cells, SBE (super-birefringence effect) cells and OMI (optical mode interference) cells. The commonest display devices are based on the Schadt-Helfrich effect and have a twisted nematic structure.

Summary of Invention Paragraph (3):
[0003] The liquid-crystal materials must have good chemical and thermal stability and good stability to electric fields and electromagnetic radiation. Furthermore, the liquid-crystal materials should have low viscosity and produce short addressing times, low threshold voltages and high contrast in the cells.

Summary of Invention Paragraph (4):
[0004] They should furthermore have a suitable mesophase, for example a nematic or cholesteric mesophase for the above-mentioned cells, at the usual operating temperatures, i.e. in the broadest possible range above and below room temperature. Since liquid crystals are generally used as mixtures of a plurality of components, it is important that the components are readily miscible with one another. Further properties, such as the electrical conductivity, the dielectric anisotropy and the optical anisotropy, have to satisfy various requirements depending on the cell type and area of application. For example, materials for cells having a twisted nematic structure should have positive dielectric anisotropy and low electrical conductivity.

Summary of Invention Paragraph (5):
[0005] For example, for matrix liquid-crystal displays with integrated non-linear elements for switching individual pixels (MLC displays), media having large positive dielectric anisotropy, broad nematic phases, relatively low birefringence, very high specific resistance, good UV and temperature stability and low vapour pressure are desired.

Summary of Invention Paragraph (6):
[0006] Matrix liquid-crystal displays of this type are known. Non-linear elements which can be used for individual switching of the individual pixels are, for example, active elements (i.e. transistors). The term "active matrix" is then used,

where a distinction can be made between two types:

Summary of Invention Paragraph (14):
[0014] MLC displays of this type are particularly suitable for TV applications (for example pocket TVs) or for high-information displays for computer applications (laptops) and in automobile or aircraft construction. Besides problems regarding the angle dependence of the contrast and the response times, difficulties also arise in MLC displays due to insufficiently high specific resistance of the liquid-crystal mixtures [TOGASHI, S., SEKIGUCHI, K., TANABE, H., YAMAMOTO, E., SORIMACHI, K., TAJIMA, E., WATANABE, H., SHIMIZU, H., Proc. Eurodisplay 84, September 1984: A 210-288 Matrix LCD Controlled by Double Stage Diode Rings, p. 141 ff, Paris; STROMER, M., Proc. Eurodisplay 84, September 1984: Design of Thin Film Transistors for Matrix Addressing of Television Liquid Crystal Displays, p. 145 ff, Paris]. With decreasing resistance, the contrast of an MLC display deteriorates, and the problem of after-image elimination may occur. Since the specific resistance of the liquid-crystal mixture generally drops over the life of an MLC display owing to interaction with the interior surfaces of the display, a high (initial) resistance is very important in order to obtain acceptable service lives. In particular in the case of low-volt mixtures, it was hitherto impossible to achieve very high specific resistance values. It is furthermore important that the specific resistance exhibits the smallest possible increase with increasing temperature and after heating and/or UV exposure. The low-temperature properties of the mixtures from the prior art are also particularly disadvantageous. It is demanded that no crystallisation and/or smectic phases occur, even at low temperatures, and the temperature dependence of the viscosity is as low as possible. The MLC displays from the prior art thus do not meet today's requirements.

Summary of Invention Paragraph (15):
[0015] In addition to liquid-crystal displays which use back-lighting, i.e. are operated transmissively and if desired transflectively, reflective liquid-crystal displays are also particularly interesting. These reflective liquid-crystal displays use the ambient light for information display. They thus consume significantly less energy than back-lit liquid-crystal displays having a corresponding size and resolution. Since the TN effect is characterised by very good contrast, reflective displays of this type can even be read well in bright ambient conditions. This is already known of simple reflective TN displays, as used, for example, in watches and pocket calculators. However, the principle can also be applied to high-quality, higher-resolution active matrix-addressed displays, such as, for example, TFT displays. Here, as already in the transmissive TFT-TN displays which are generally conventional, the use of liquid crystals of low birefringence (.DELTA.n) is necessary in order to achieve low optical retardation (d.multidot..DELTA.n). This low optical retardation results in usually acceptable low viewing-angle dependence of the-contrast (cf. DE 30 22 818). In reflective displays, the use of liquid crystals of low birefringence is even more important than in transmissive displays since the effective layer thickness through which the light passes is approximately twice as large in reflective displays as in transmissive displays having the same layer thickness.

Summary of Invention Paragraph (25):
[0025] The invention has an object of providing media, in particular for MLC, TN or STN displays of this type, which do not have the above-mentioned disadvantages or only do so to a reduced extent, and preferably simultaneously have very high specific resistances and low threshold voltages. This object requires liquid-crystalline compounds which have a high clearing point and low rotational viscosity. Upon further study of the specification and appended claims, further objects and advantages of this invention will become apparent to those skilled in the art.

Summary of Invention Paragraph (26):
[0026] It has now been found that these and other objects can be achieved if use is made of the liquid-crystalline compound which has a terminal polar radical and a terminal CH.sub.3 group. The compounds of the formula I reduce the elastic constants, in particular K.sub.1, and result in mixtures having particularly low threshold voltages.

Summary of Invention Paragraph (27):
[0027] The invention thus relates to a liquid-crystalline medium based on a mixture of polar compounds of positive or negative dielectric anisotropy, comprising one or more compounds of the formula 3

Summary of Invention Paragraph (40):
[0040] In the pure state, the compounds of the formula I are colorless and generally form liquid-crystalline mesophases in a temperature range which is favorably located for electro-optical use. In particular, the compounds according to the invention are distinguished by their high clearing point and low rotational viscosity values. They are stable chemically, thermally and to light. 6

Summary of Invention Paragraph (67):
[0054] The compounds of the formula I are prepared by methods known per se, as described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for the said reactions. Use can also be made here of variants which are known per se, but are not mentioned here in greater detail. Liquid-crystalline compounds having a CF.sub.2O bridge or C.sub.2F.sub.4 bridge can be prepared, for example, as described in P. Kirsch et al., Angew. Chem. 2001, 113, 1528-1532 or 2001, 123, 5414-5417.

Summary of Invention Paragraph (69):
[0056] The invention also relates to electro-optical displays (in particular STN or MLC displays having two plane-parallel outer plates, which, together with a frame, form a cell, integrated non-linear elements for switching individual pixels on the outer plates, and a nematic liquid-crystal mixture of positive dielectric anisotropy and high specific resistance which is located in the cell) which contain media of this type, and to the use of these media for electro-optical purposes.

Summary of Invention Paragraph (70):
[0057] The liquid-crystal mixtures according to the invention enable a significant widening of the available parameter latitude.

Summary of Invention Paragraph (72):
[0059] The requirement for a high clearing point, a nematic phase at low temperature and a high .DELTA..di-elect cons. has hitherto only been achieved to an inadequate extent. Although liquid-crystal mixtures such as, for example, MLC-6476 and MLC-6625 (Merck KGaA, Darmstadt, Germany) have comparable clearing points and low-temperature stabilities, they have, however, relatively low .DELTA.n values and also higher threshold voltages of about .gtoreq.1.7 V..

Summary of Invention Paragraph (74):
[0061] The liquid-crystal mixtures according to the invention, while retaining the nematic phase down to -20.degree. C. and preferably down to -30.degree. C., particularly preferably down to -40.degree. C., enable clearing points above 80.degree. C., preferably above 90.degree. C., particularly preferably above 100.degree. C., simultaneously dielectric anisotropy values .DELTA..di-elect cons. of .gtoreq.4, preferably .gtoreq.6, and a high value for the specific resistance to be achieved, enabling excellent STN and MLC displays to be obtained. In particular, the mixtures are characterised by low operating voltages. The TN thresholds are below 1.5 V., preferably below 1.3 V.

Summary of Invention Paragraph (77):
[0064] Measurements of the capacity holding ratio (HR) [S. Matsumoto et al., Liquid Crystals 5, 1320 (1989); K. Niwa et al., Proc. SID Conference, San Francisco, June 1984, p. 304 (1984); G. Weber et al., Liquid Crystals 5, 1381 (1989)] have shown that mixtures according to the invention comprising compounds of the formula I exhibit a significantly smaller decrease in the HR with increasing temperature than, for example, analogous mixtures comprising cyanophenylcyclohexanes of the formula 18

Summary of Invention Paragraph (118):
[0105] It has been found that even a relatively small proportion of compounds of the formula I mixed with conventional liquid-crystal materials, but in particular with

one or more compounds of the formulae II, III, IV, V, VI, VII, VIII, IX and/or X, results in a significant lowering of the threshold voltage and in low birefringence values, with broad nematic phases with low smectic-nematic transition temperatures being observed at the same time, improving the shelf life. The compounds of the formulae I to X are colorless, stable and readily miscible with one another and with other liquid-crystalline materials.

Summary of Invention Paragraph (130):
[0117] A significant difference between the displays according to the invention and the conventional displays based on the twisted nematic cell consists, however, in the choice of the liquid-crystal parameters of the liquid-crystal layer.

Summary of Invention Paragraph (131):
[0118] The liquid-crystal mixtures which can be used in accordance with the invention are prepared in a manner conventional per se. In general, the desired amount of the components used in the lesser amount is dissolved in the components making up the principal constituent, advantageously at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again, for example by distillation, after thorough mixing.

Summary of Invention Paragraph (136):
[0123] In the present application and in the examples below, the structures of the liquid-crystal compounds are indicated by means of acronyms, the transformation into chemical formulae taking place in accordance with Tables A and B below. All radicals C.sub.nH.sub.2n+1 and C.sub.mH.sub.2m+1 are straight-chain alkyl radicals having n and m carbon atoms respectively; n and m are in each case, independently of one another, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15. The coding in Table B is self-evident. In Table A, only the acronym for the parent structure is indicated. In individual cases, the acronym for the parent structure is followed, separated by a dash, by a code for the substituents R.sup.1, R.sup.2, L.sup.1 and L.sup.2:

Summary of Invention - Table CWU (3):
3TABLE B 57 CBC-nmF 58 PCH-nOm 59 FET-nCl 60 CP-nOCF.sub.3 61 CCH-nOm 62 BCH-n.FX 63 Inm 64 CBC-nmF 65 ECCP-nm 66 CCH-n1EM 67 T-nFm 68 CGU-n-F 69 CCP-nOCF.sub.3.F 70 CGG-n-F 71 CCP-nOCF.sub.2.F(.F) 72 CCP-nF.F.F 73 CGU-n-OXF 74 CUZU-n-F 75 CGU-n-O1DT 76 CCZU-n-F 77 CC-n-V1 78 CC-n-V 79 CCP-nOCF.sub.3 80 BCH-nF.F.F 81 CWCZU-n-F 82 CWCZG-n-F 83 CCOC-n-m 84 CGZU-n-F 85 CUZP-n-F 86 CGU-1V-F 87 CCG-V-F 88 CGZP-n-F 89 UZP-n-N 90 CGZP-n-OT 91 CUZP-n-OT 92 CCQU-n-F 93 Dec-U-n-F 94 Nap-U-n-F 95 CWGZG-n-F 96 CWCZG-n-OT 97 CWCZP-n-OT 98 CWCQU-n-F 99 CCP-nF.F

CLAIMS:

1. A liquid-crystalline medium comprising a mixture of polar compounds of positive or negative dielectric anisotropy, including one or more compounds of the formula I 105in which 106are a) a 1,4-cyclohexenylene or 1,4-cyclohexylene radical, in which one or two non-adjacent CH.sub.2 groups are optionally replaced by --O-- or --S--, b) a 1,4-phenylene radical, in which one or two CH groups are optionally replaced by N, c) a radical selected from the group consisting of piperidine-1,4-diyl, 1,4-bicyclo[2.2.2]octylene, naphthalene-2,6-diyl, decahydronaphthalene-2,- 6-diyl, 1,2,3,4-tetrahydronaphthalene-2,6-diyl, phenanthrene-2,7-diyl and fluorene-2,7-diyl, where the radicals a), b) and c) are optionally monosubstituted or polysubstituted by halogen atoms, 107x, y and z are each, independently of one another, 0, 1 or 2, Z.sup.1, Z.sup.2 and Z.sup.3 are each, independently of one another, --CO--O--, --O--CO--, --CF.sub.2O--, --OCF.sub.2--, --CH.sub.2O--, --OCH.sub.2--, --CH.sub.2CH.sub.2--, --(CH.sub.2).sub.4--, --C.sub.2F.sub.4--, --CH.sub.2CF.sub.2--, --CF.sub.2CH.sub.2--, --CF.dbd.CF--, --CH.dbd.CH--, --C.ident.C-- or a single bond, X is F, Cl, CN, SF.sub.5, NCS, a halogenated or unsubstituted alkyl radical having 1 to 8 carbon atoms, in which one or more CH.sub.2 groups are optionally replaced by --O-- or --CH.dbd.CH-- in such a way that O atoms are not linked directly to one another, a is 0, 1 or 2 b is 0, 1 or 2, and c is 0, 1 or 2, where a+b+c is .ltoreq.3.

2. A liquid-crystalline medium according to claim 1, wherein X in the formula I is F, Cl, CN, NCS, CF.sub.3, C.sub.2F.sub.5, n--C.sub.3F.sub.7, SF.sub.5, CF.sub.2H,

OCF.sub.3, OCF.sub.2H, OCFHCF.sub.3, OCFHCFH.sub.2, OCFHCF.sub.2H, OCF.sub.2CH.sub.3, OCF.sub.2CFH.sub.2, OCF.sub.2CF.sub.2H, OCF.sub.2CF.sub.2CF.sub.2H, OCF.sub.2CF.sub.2CFH.sub.2, OCFHCF.sub.2CF.sub.3, OCFHCF.sub.2CF.sub.2H, OCF.sub.2CF.sub.2CF.sub.3, CF.sub.2CHFCF.sub.3, CF.sub.2CH.sub.2CF.sub.3, OCH.sub.2CF.sub.2CHFCF.sub- .3, OCF.sub.2CHFCF.sub.3, OCClFCF.sub.2CF.sub.3, CH.sub.3, C.sub.2H.sub.5 and n--C.sub.3H.sub.7.

3. A liquid-crystalline medium according to claim 1, which comprises at least one compound from the group consisting of the compounds of the formulae I1 to I31: 108109110111in which X is as defined in claim 1, alkyl is a straight-chain or branched alkyl radical having 1-8 carbon atoms, and L.sup.1 to L.sup.2 are each, independently of one another, H or F.

4. A liquid-crystalline medium according to claim 1, which additionally comprises one or more compounds selected from the group consisting of those of formulae II, III, IV, V, VI, VII, VIII, IX and X: 112113in which the individual radicals have the following meanings: R.sup.0 is n-alkyl, oxaalkyl, fluoroalkyl, alkenyloxy or alkenyl, each having from 2 to 12 carbon atoms X.sup.0 is F, Cl, halogenated alkyl, halogenated alkenyl, halogenated alkenyloxy or halogenated alkoxy, each having 1 to 8 carbon atoms, Z.sup.0 is --CH.dbd.CH--, --CH.sub.2O--, --OCH.sub.2--, --(CH.sub.2).sub.4--, --C.sub.2H.sub.4--, --C.sub.2F.sub.4--, --CF.dbd.CF--, --CF.sub.2O--, --OCF.sub.2-- or --COO--, Y.sup.1, Y.sup.2, Y.sup.3 and Y.sup.4 are each, independently of one another, H or F, and r is 0 or 1.

5. A liquid-crystalline medium according to claim 4, wherein the proportion of compounds of the formulae I to X in the medium as a whole is at least 50% by weight.

6. A liquid-crystalline medium according to claim 1, which additionally comprises one or more compounds of the formulae RI to RXIV: 114115in which R.sup.0 is n-alkyl, oxaalkyl, fluoroalkyl, alkenyloxy or alkenyl, each having from 2 to 8 carbon atoms, d is 0, 1 or 2, Y.sup.1 is H or F, alkyl and alkyl* are each, independently of one another, a straight-chain or branched alkyl radical having from 2 to 8 carbon, atoms, alkenyl and alkenyl* are each, independently of one another, a straight-chain or branched alkenyl radical having from 2 to 8 carbon atoms.

7. A liquid-crystalline medium according to claim 4, comprising at least one compound wherein X.sup.0 is F, OCHF.sub.2 or OCF.sub.3, and Y.sup.2 is H or F.

8. Electro-optical liquid-crystal display containing a liquid-crystalline medium according to claim 1.

9. The liquid-crystalline medium of claim 1, wherein the medium exhibits a nematic phase down to -20.degree. C., a clearing point above 80.degree. C., a dielectric anisotropy, .DELTA..di-elect cons., of .gtoreq.4.

10. The liquid-crystalline medium of claim 9, wherein the medium exhibits a TN threshold below 1.5 V.

11. The liquid-crystalline medium of claim 9, wherein the medium exhibits a flow viscosity, .nu..sub.20, at 20.degree. C. of <60 mm.sup.2.multidot.s.sup.-1 and a nematic phase range of at least 90.degree..

12. The liquid-crystalline medium of claim 1, wherein the proportion of compounds of formula I in the medium is from 5 to 50% by weight.

13. The liquid-crystalline medium of claim 1, wherein the medium additionally comprises one or more compounds selected from the group consisting of compounds of the formulae XI to XVI: 116in which R.sup.0 is n-alkyl, oxaalkyl, fluoroalkyl, alkenyloxy or alkenyl, each having from 2 to 8 carbon atoms, Y.sup.1-Y.sup.4 are, independently, H or F, and X.sup.0 is F, Cl, halogenated alkyl, halogenated alkenyl, halogenated alkenyloxy or halogenated alkoxy, each having up to 8 carbon atoms.

14. The liquid-crystalline medium of claim 4, wherein the medium additionally comprises one or more compounds selected from the group consisting of compounds of

the formulae XI to XVI: 117in which R.sup.0 is n-alkyl, oxaalkyl, fluoroalkyl, alkenyloxy or alkenyl, each having from 2 to 8 carbon atoms, Y.sup.1-Y.sup.4 are, independently, H or F, and X.sup.0 is F, Cl, halogenated alkyl, halogenated alkenyl, halogenated alkenyloxy or halogenated alkoxy, each having up to 8 carbon atoms.